Relativistic and quasirelativistic electronic structure calculations on the alkali metal - rare gas molecules

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The accurate estimates of spectroscopic, kinetic and thermodynamic properties of the weakly bound diatomic pairs formed in interactions of alkali metal vapors and inert buffer gas are indispensably required to construct and operate high-power optically pumped lasers [1]. The state-of-art quantum chemistry machinery provides both interatomic adiabatic potential energy curves (PECs) and transition dipole moments (TDMs) which reproduce the observed spectroscopic and radiative properties of many diatomic molecules with accuracy close or comparable to experimental one.

At the present work we have performed, in the framework of high level ab initio electronic structure calculations, a comparative study of the full relativistic and quasirelativistic affects on energies and electronic transitions probabilities between the ground and low-lying excited states of the exciplex RbAr and CsAr molecules. The different sets of small core relativistic pseudopotentials were used to account for both scalar and spin-dependent (spin-orbit) relativistic effects. The core-valence correlation was included in the quasirelativistic treatment by means of a large-scale multi-reference configuration interaction (MR-CI) method. The alternative full relativistic calculations employed the Fock-space coupled clusters (FS-CC) method. The finite-field (FF) method was applied for evaluating the corresponding TDM functions within the FS-CC theory [2].

Peculiarities in a shape of the resulting PECs and TDM functions revealed at intermediate and large interatomic distance were discussed. The reliability of the derived PECs and TDM functions were accessed through a comparison with previous theoretical and experimental results. The present *ab initio* data have been used to simulate the absorption spectra for RbAr and CsAr pairs as well as radiative lifetimes of the excited states in the framework of semiclassical approximation.

[1] D.L. Carroll and J.T. Verdeyen, *J. Phys. B*, **46**, 025402 (2013).

[2] A. A. Medvedev, A. V. Stolyarov, A. Zaitsevskii, and E. Eliav, *Nonlin. Phenom. Complex Sy*st. **20**, 205 (2017).